

# AC-Induced Bias Potential Effect on Corrosion of Steels

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**Feb. 5, 2009**



Report Documentation Page				Form Approved OMB No. 0704-0188	
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1. REPORT DATE <b>05 FEB 2009</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2009 to 00-00-2009</b>	
4. TITLE AND SUBTITLE <b>AC-Induced Bias Potential Effect on Corrosion of Steels</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Generation 2 Materials Technology LLC,10281 Foxfire St,Firestone,CO,80504</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>2009 U.S. Army Corrosion Summit, 3-5 Feb, Clearwater Beach, FL</b>					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>37</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

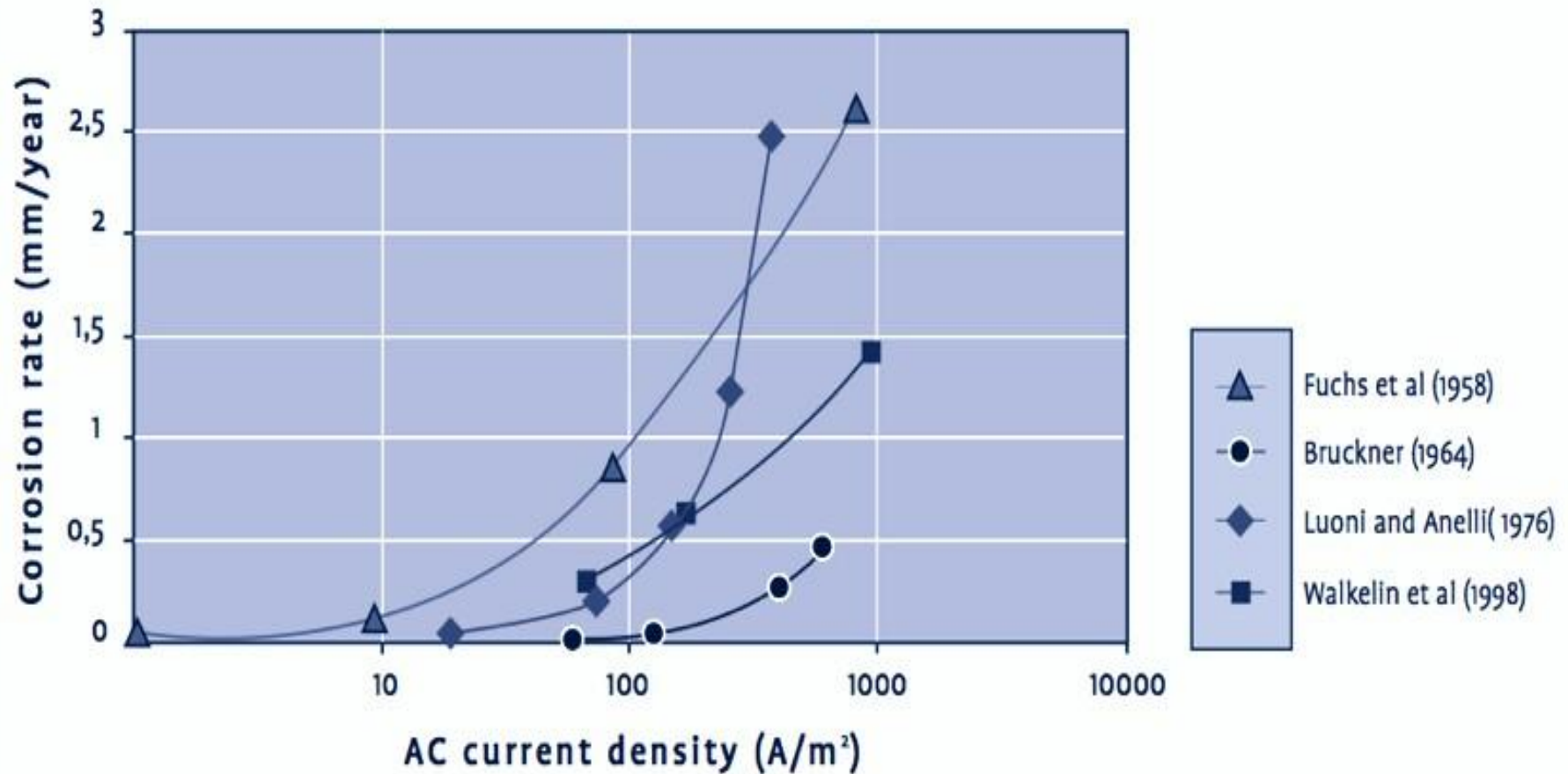
# Overview

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# Background/Motivation

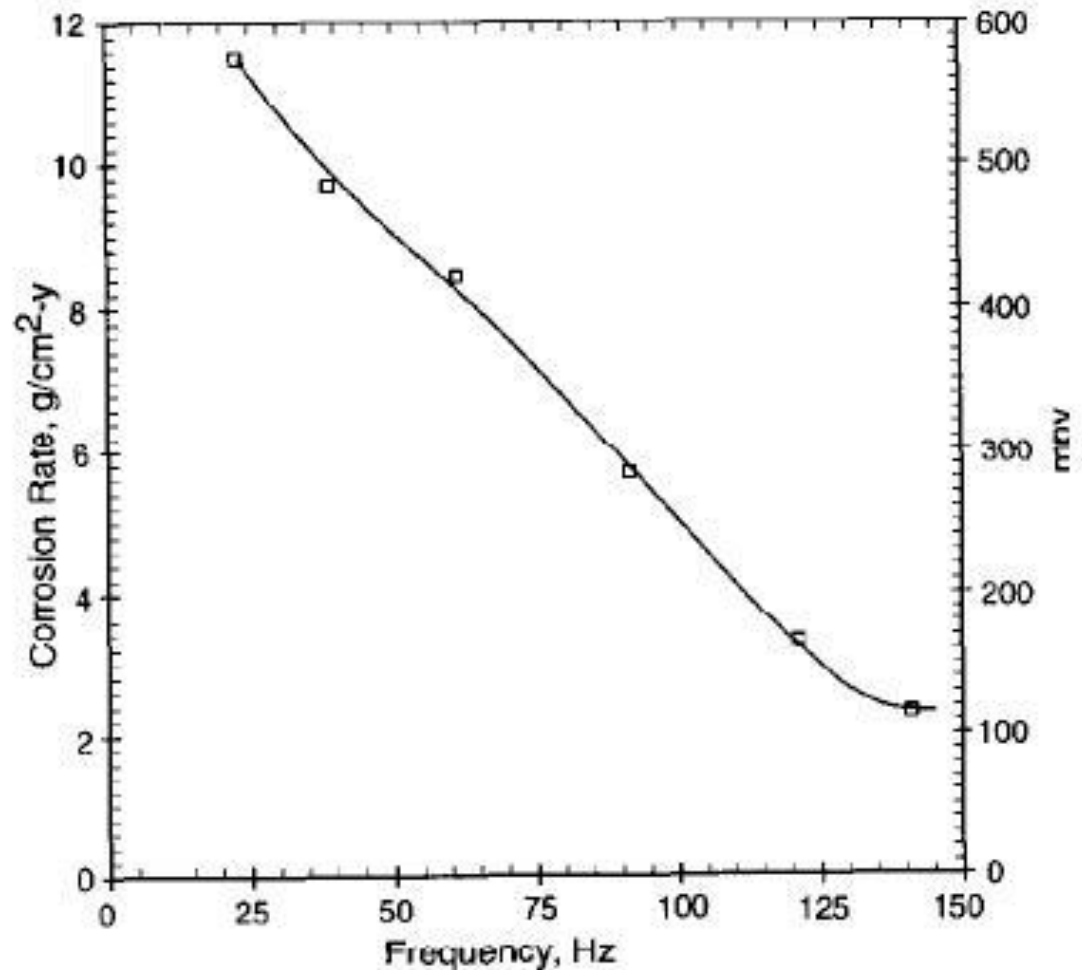
- **Increased use of AC electric power in a wide variety of DoD applications increases the probability of AC corrosion damage**
- **The nature and mechanisms of AC corrosion damage need to be firmly established to allow predictability of AC corrosion susceptibility**
- **Long-term effects of AC on the integrity of systems is unknown and needs to be established for prediction of service life**
- **CSM-DOT-DOI JIP found significant increase in corrosion, including hydrogen content, pitting, and cracking, of pipeline steels in presence of a magnetic field in lab [Jackson et al., 2006]**

# Effect of AC Current Density



# Effect of AC Frequency

- Suggests that one solution is to change the frequency of AC power to reduce corrosion damage



**Figure 8 – Corrosion Rate of 1018 Carbon Steel in a 3.3% NaCl Solution vs. Frequency at an AC Peak Potential of 180mV**  
(Lalvani and Zhang, 1995) <sup>[44]</sup>

# AC/DC Corrosion Map

- AC current alters protection of systems using cathodic protection
- AC current density will be very high at defects and holes

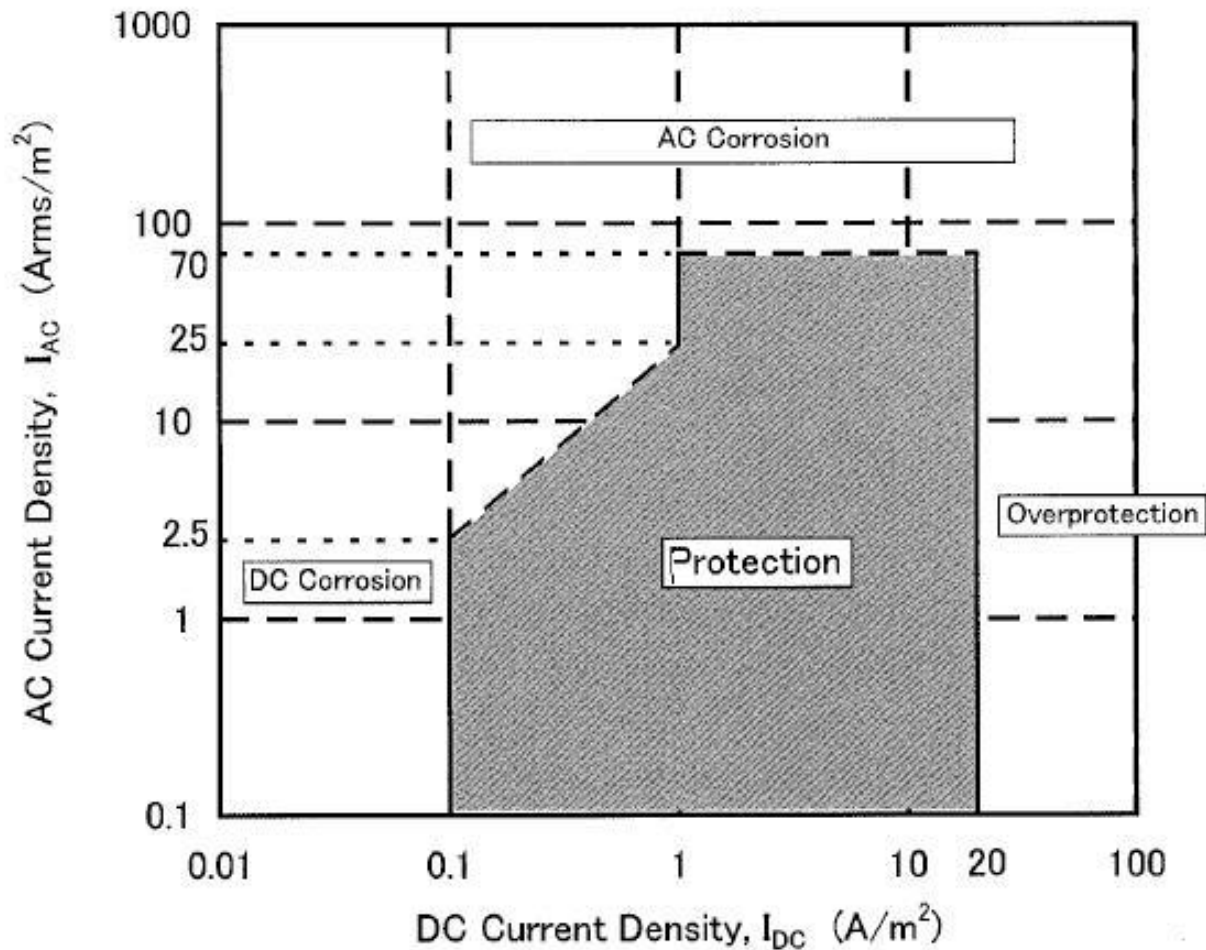
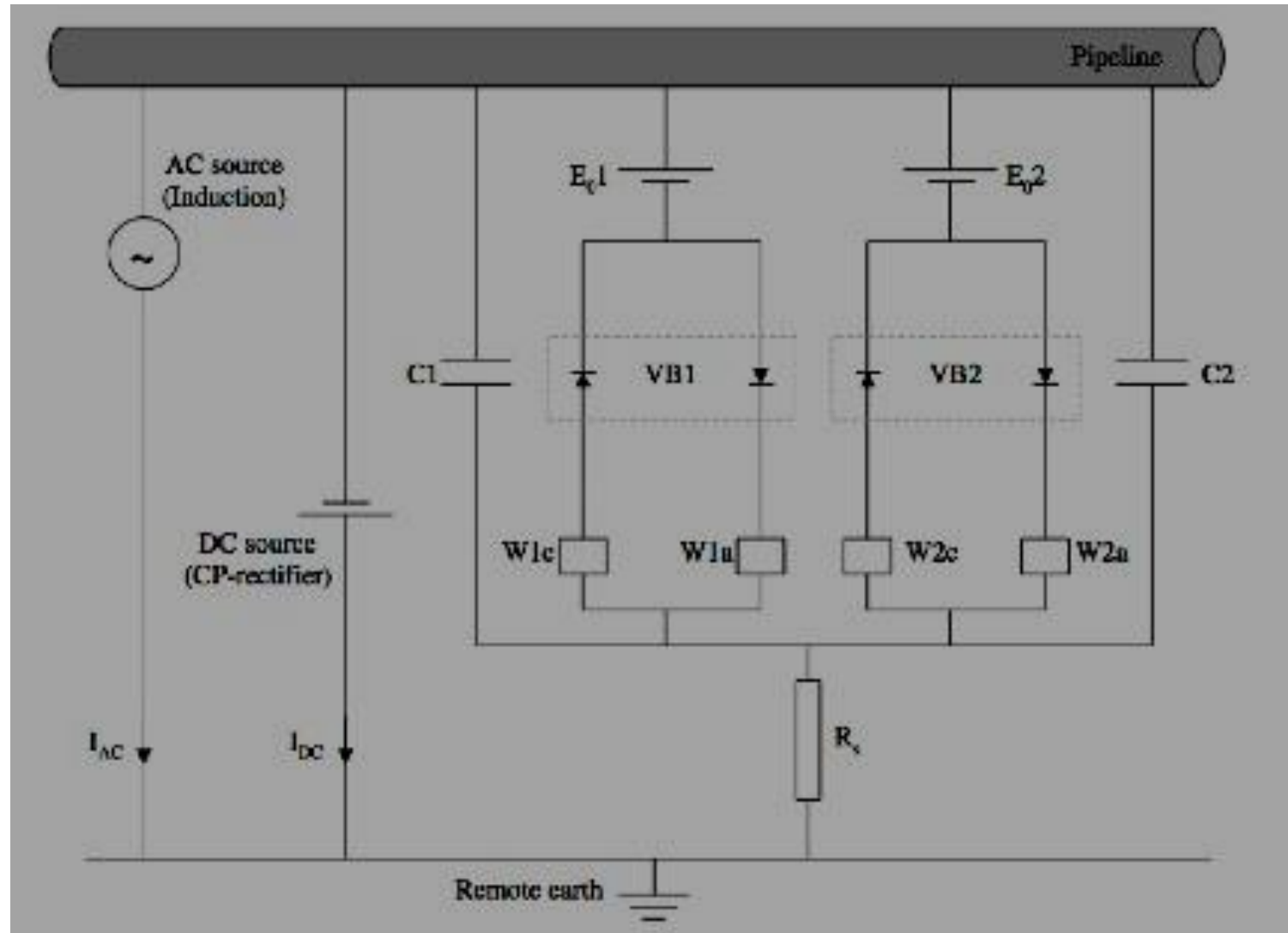


Figure 1. Graphic illustration of the cathodic protection criteria for buried steel pipelines based on DC and AC current densities measured using coupons.

# Electronic Model of Pits (Nielsen)

**Electronic model of two pits with different voltages, etc.**

**Pit is a hole in coating, which allows different reactions relative to AC current**



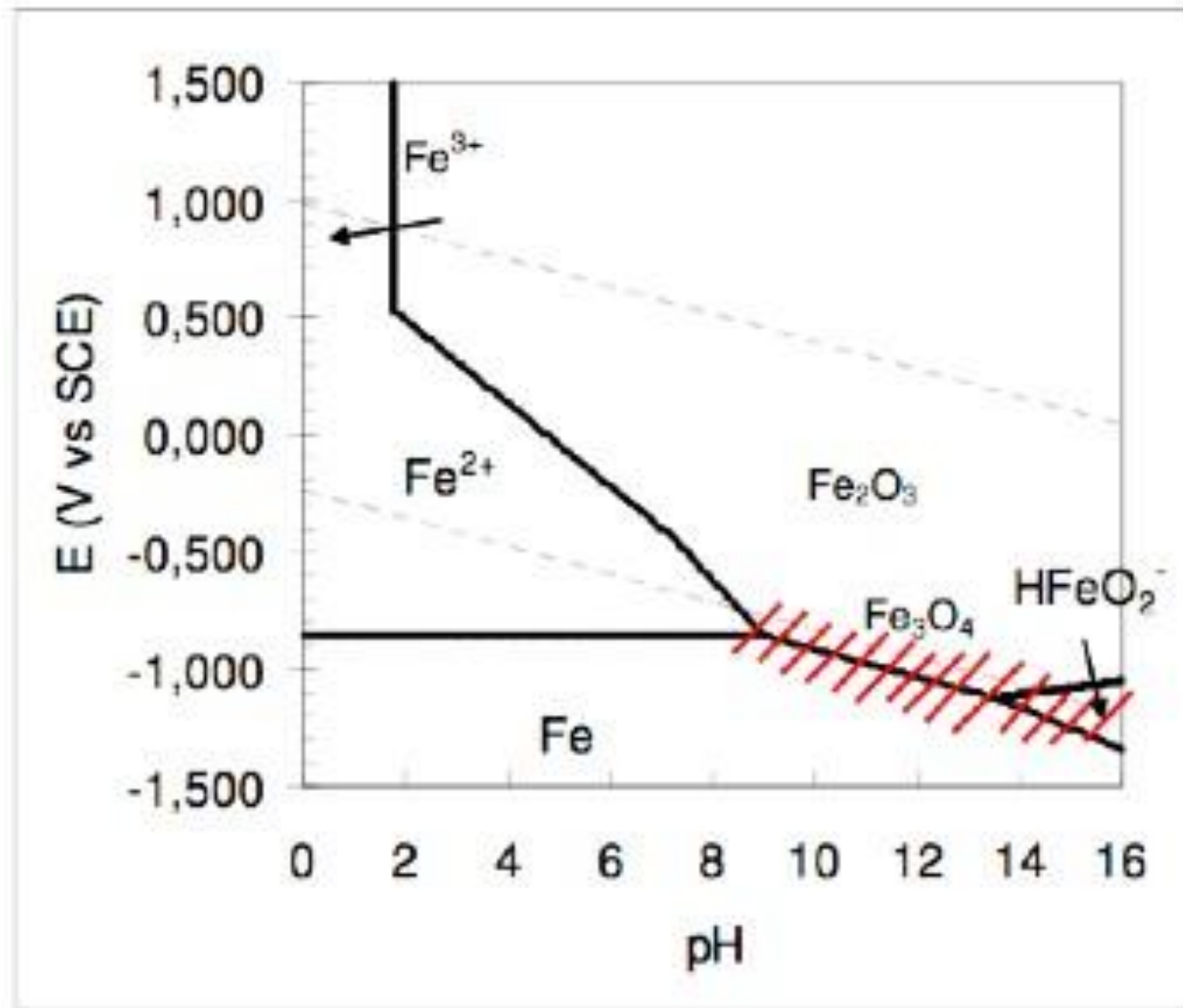
Schematic illustration of the electrical equivalent circuit for AC-corrosion as proposed by Nielsen and Cohn (2000).



# Pourbaix Diagram (Nielsen)

AC corrosion is promoting a strong cathode behavior which pulls out hydrogen ions out of pits and making hydrogen gas

- Then hydroxyl ions make up difference to satisfy equilibrium equation, so more OH's are made (mainly in coating pits)



Pourbaix-diagram showing dangerous region in respect to AC induced corrosion (as proposed by Nielsen, et al., 2006)

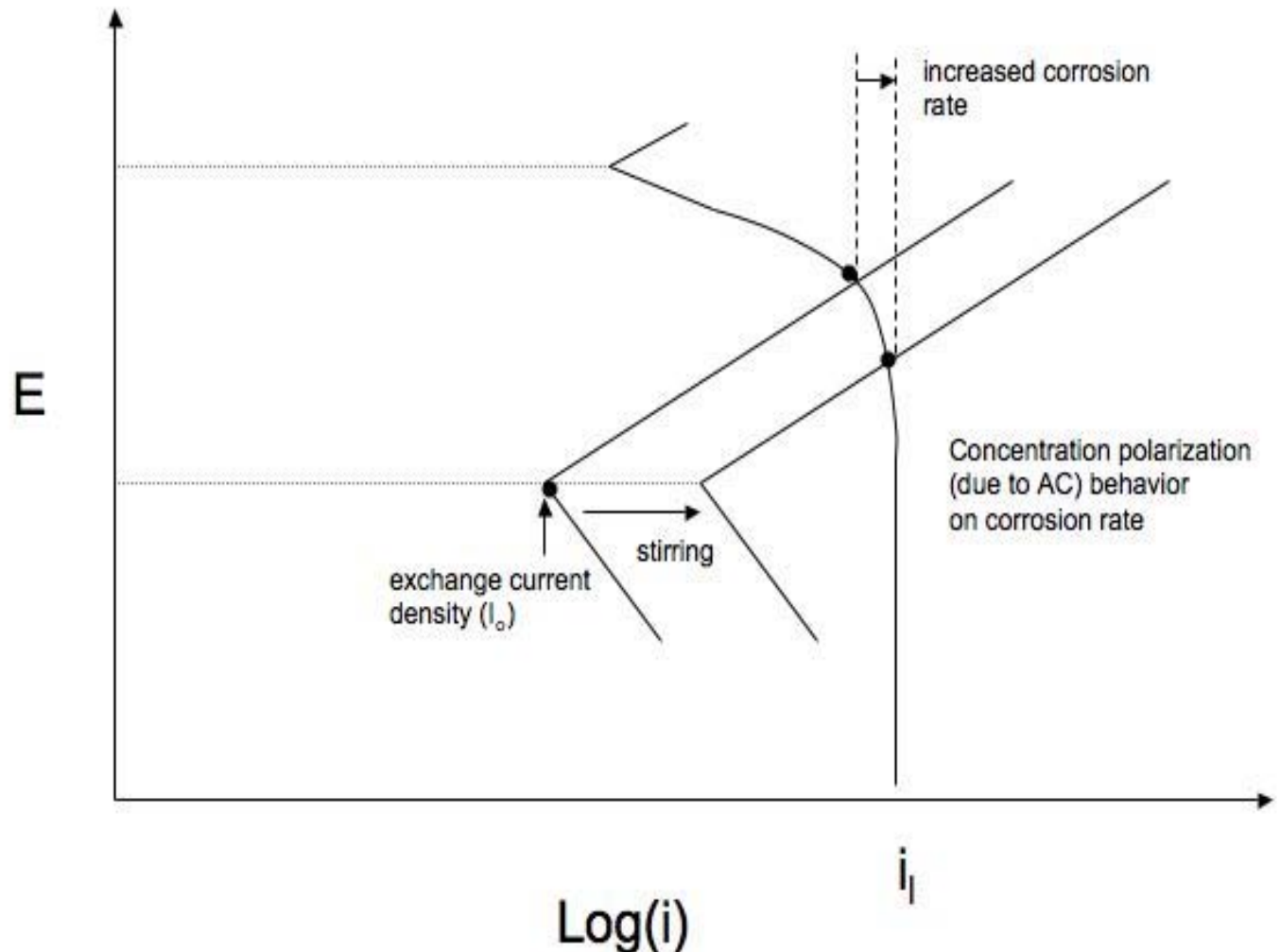
# Alkalization *Model 1*

- **DC stray current:**
  - **Potential lowered (more cathodic) where the current enters the pipeline**
  - **Potential increased (more anodic) where DC exits the pipeline (increasing risk of corrosion)**
  - **DC stray current avoided by adding an excess of CP**
- **AC stray current:**
  - **Excess CP fatal due to an unexpected increase in pH at coating faults**
  - **CP current produces  $\text{OH}^-$  ions (Galsgaard, 2006)**

# AC Corrosion in Pits (Bosch & Bogaerts)

**Bosch and Bogaerts (1998) found:**

- AC corrosion sensitive to Tafel parameters
- Concentration polarization in the pit causes a measured drop in voltage
- limited by the diffusion-limited current density.

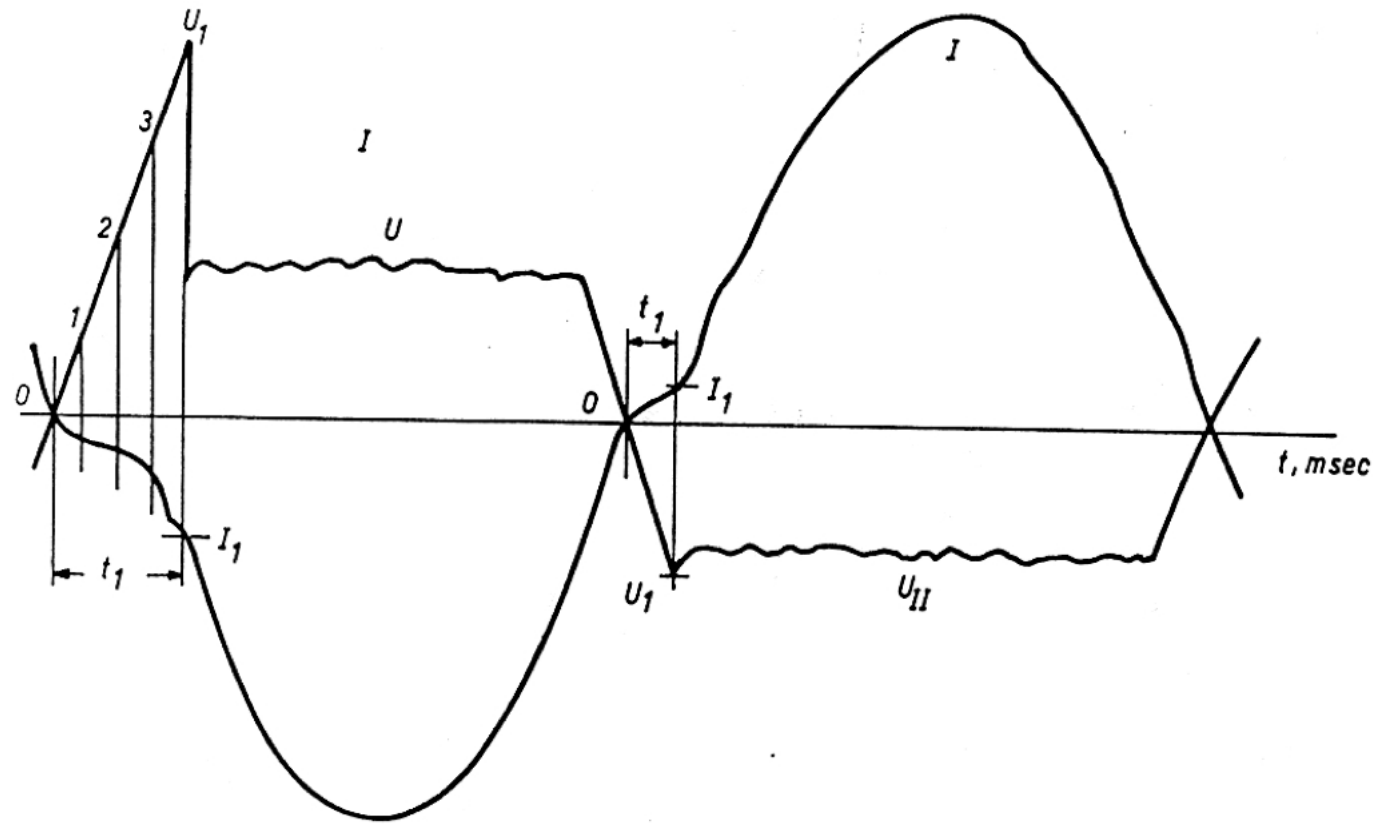


AC corrosion rate increases due to stirring in the near surface electrolyte by an increase in exchange current density of the anode reaction, and can experience diffusion-limited current density,  $i_l$ .

# AC Passive Layer Rectification *Model 2*

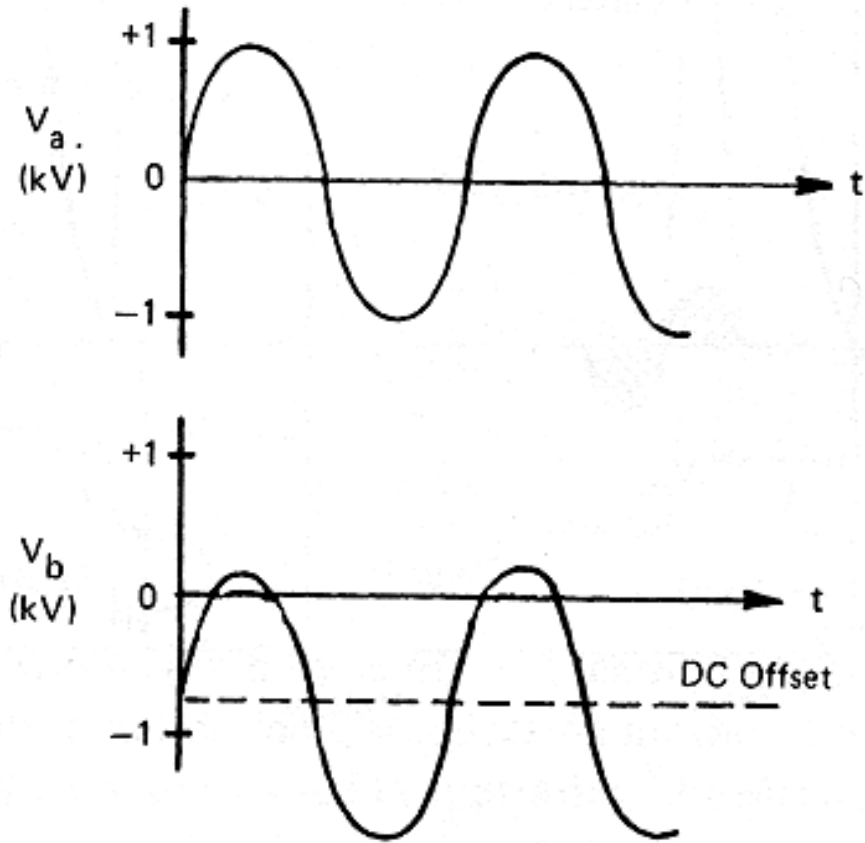
- A typical AC welding cycle for AC welding of passive alloy will produce a asymmetry.

- Possibly apply to AC corrosion where asymmetric currents lead to rectification or stripping of passive layer.

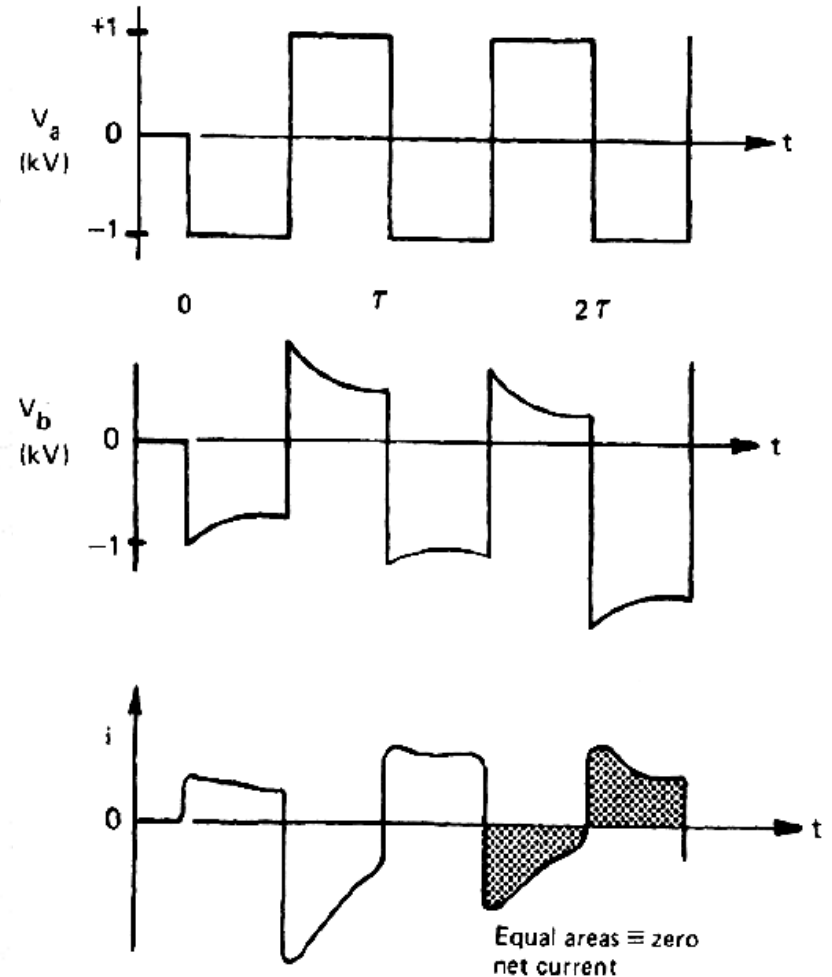


AC arc parameter changes in (I) positive and (II) negative half-cycles, causing asymmetric surface potential phenomena (Pokhodnaya, 1991).

# AC Self-biasing (from RF) *Model 3*



Voltage waveforms at generator ( $V_a$ ) and target ( $V_b$ ) in sinusoidally-excited rf discharge (Chapman, 1980).



Voltage and target current waveforms when a high frequency glow discharge circuit is square wave excited (Chapman, 1980).

# Measured AC Corrosion Kinetics

Shift is indicative of another potential (bias potential) acting on the system

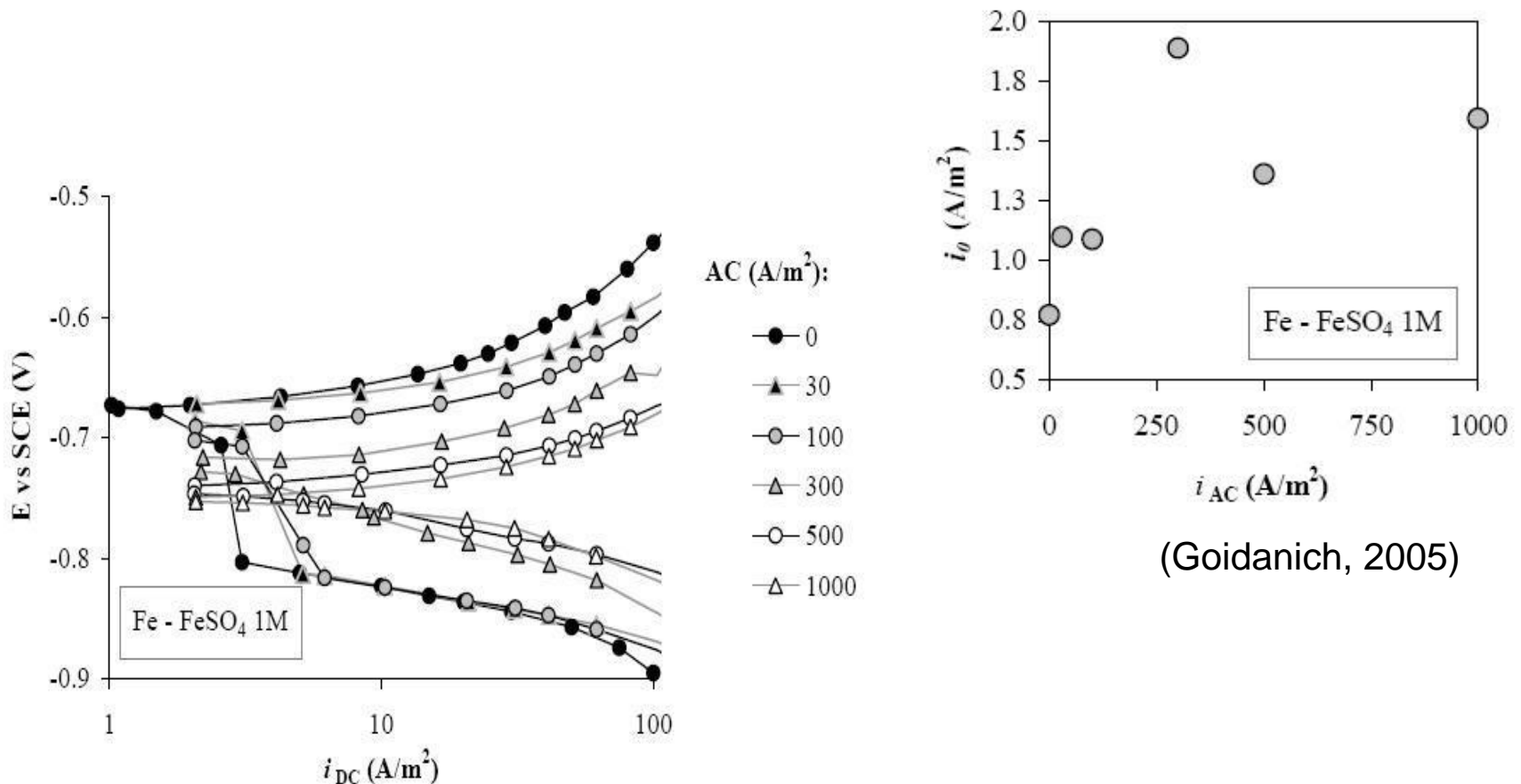
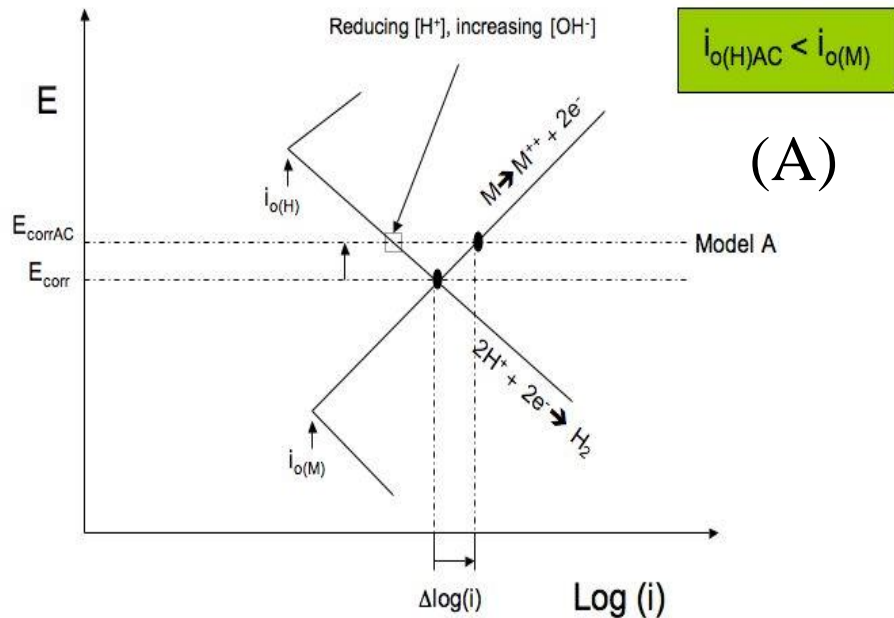


FIGURE 4 – Effect of AC (0–1,000 A/m<sup>2</sup>) on polarization curves of carbon steel (Fe) in FeSO<sub>4</sub>1 M

# AC Self-biasing *Model 3*

(A) Enhanced corrosion and possible increased alkalinity



(B) Enhanced hydrogen egress into the steel.

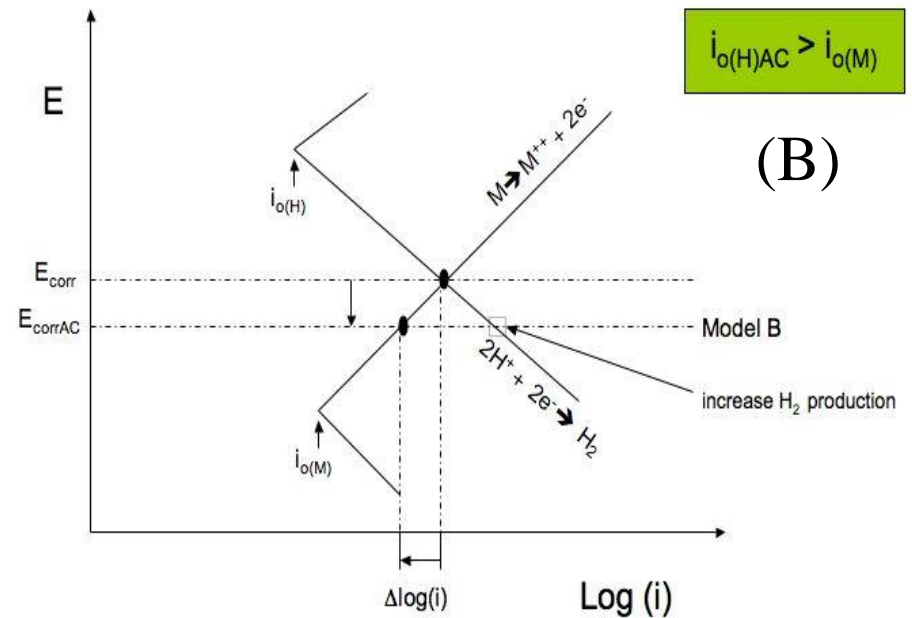
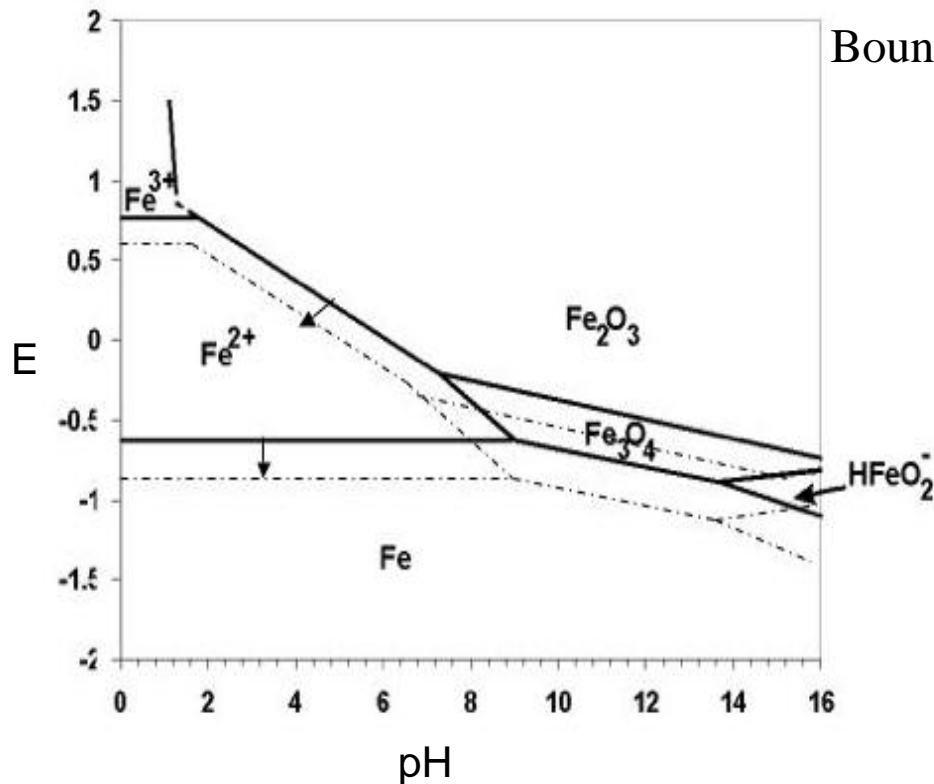


Figure 9. The self-bias phenomena due to AC behavior for a typical active metal

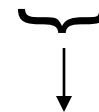
# AC Self-biasing *Model 3*



Boundary lines derived from the Nernst equation:

$$\Delta G = -nfE - nq(\Delta V) \quad (1)$$

$$E = E_o - RT \ln(\text{activities}) - nq(\Delta V) \quad (2)$$



Additional external work term due to a shift in surface potential due to asymmetrical AC behavior



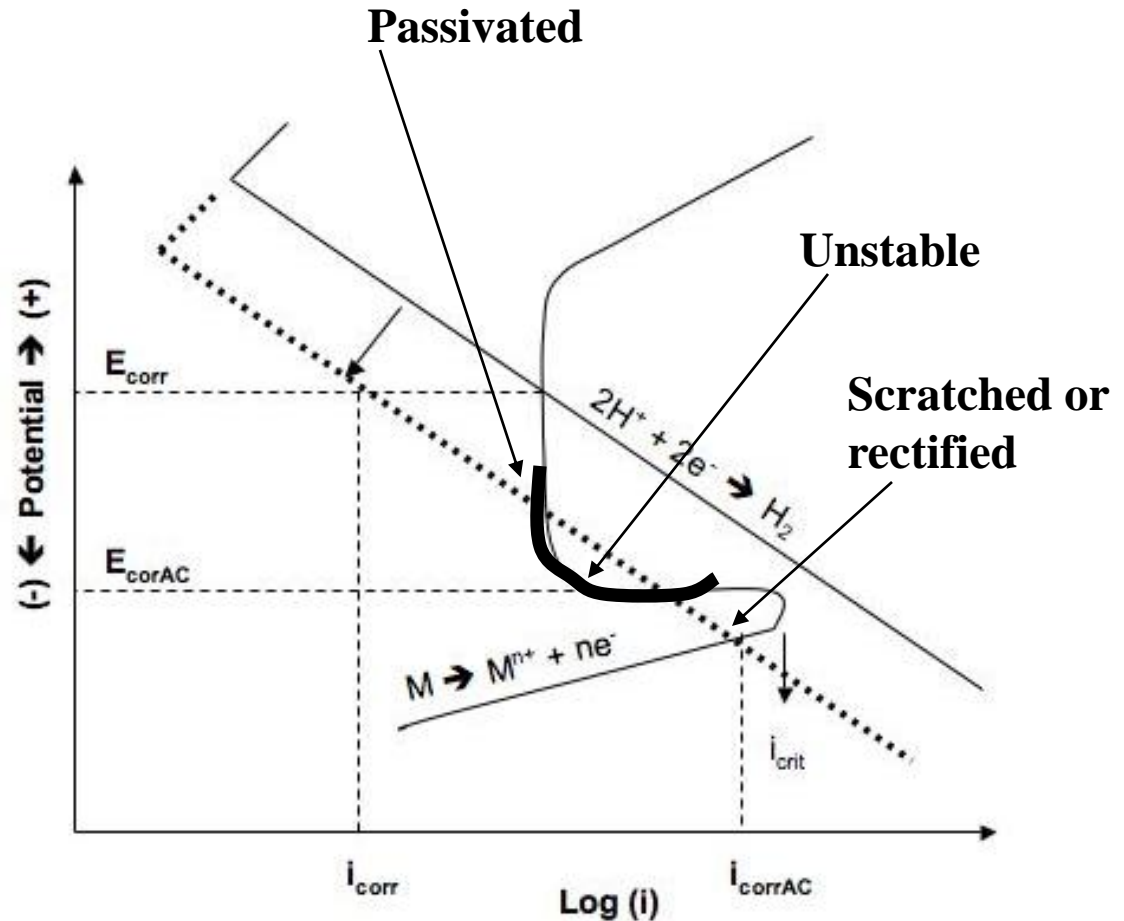
Shift of all lines associated with an electrochemical half-cell reaction

Pourbaix-diagram (potential vs. pH) showing shift in boundary lines due to a shift in potential resulting from applied AC.



# AC Self-biasing *Model 3b* for stainless

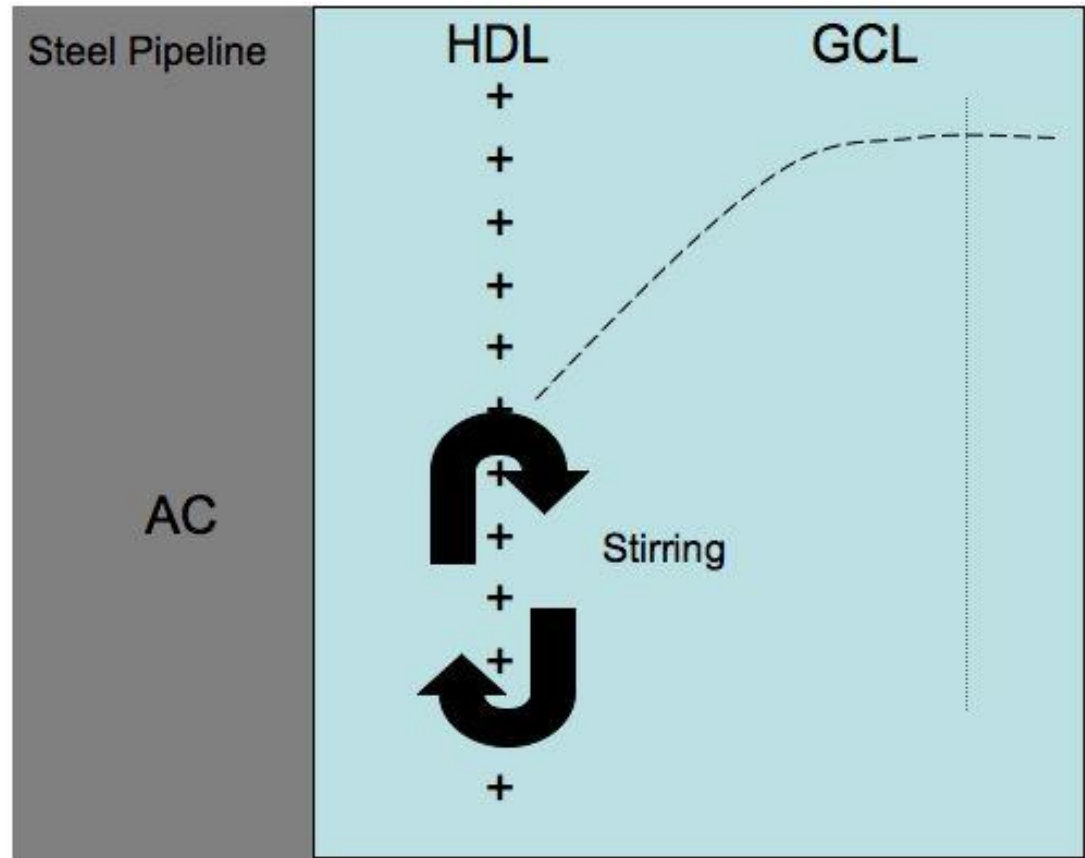
- Shift in potential resulting in shift from the passive region to an active region
- Increase corrosion rate by orders of magnitude if cathode line shifts to intersect active anode line
- For stainless and passivating alloys which previously formed passive film, damaged as a result of AC rectification



Evans diagram showing the effect of self-bias phenomena due to AC behavior for a typical passive metal.

# AC Surface Layer Stirring *Model 4*

- Stirring of the Helmholtz and the Gouy-Chapman layers due to AC fields
- A result of rapid changes of the self-generated magnetic field (Lenz's Law)



**Schematic of AC surface stirring model.**

# Electromagnetic stirring *Model 4*

- Interface potential at charged surface is proportional to number of ions attached at surface (+ & -)
- Potential and kinetic energies affect thickness and diffusivity of the surface layer

**Electromagnetic fields disturb the HDL and GCL surface layers and cause increased hydrogen diffusion**

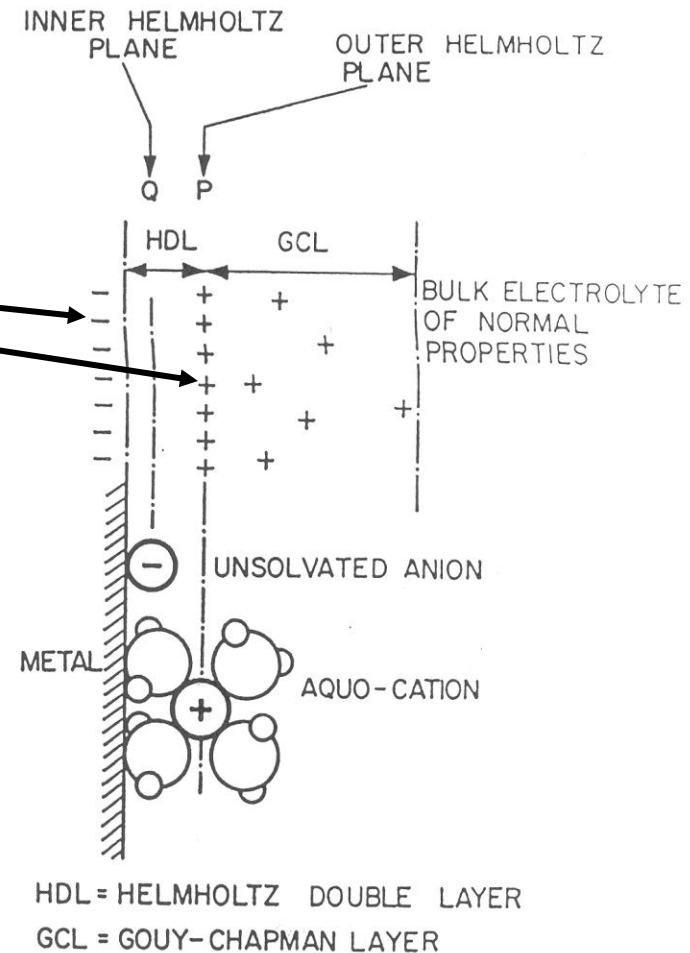
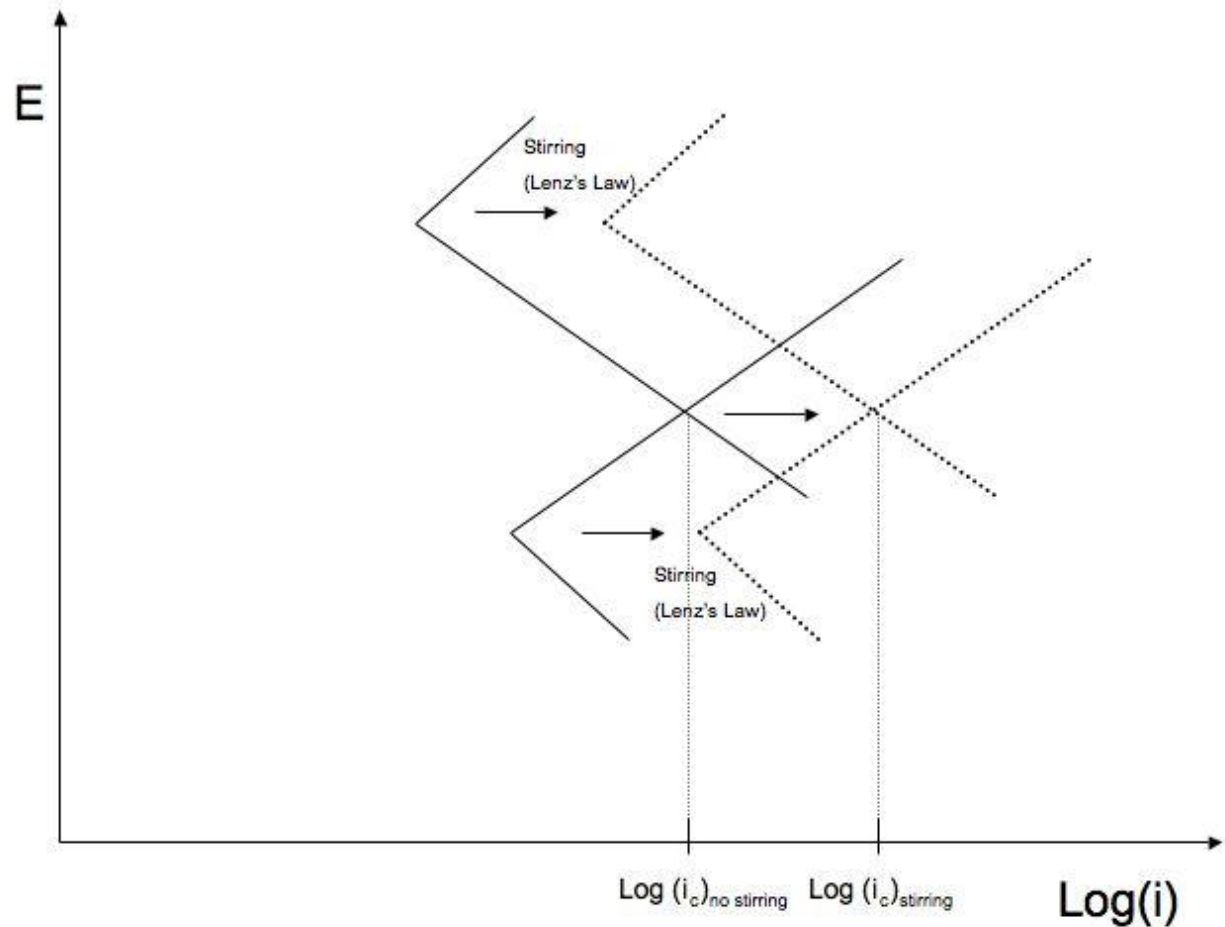


FIG. 1.4 The structure of the electrical double layer.

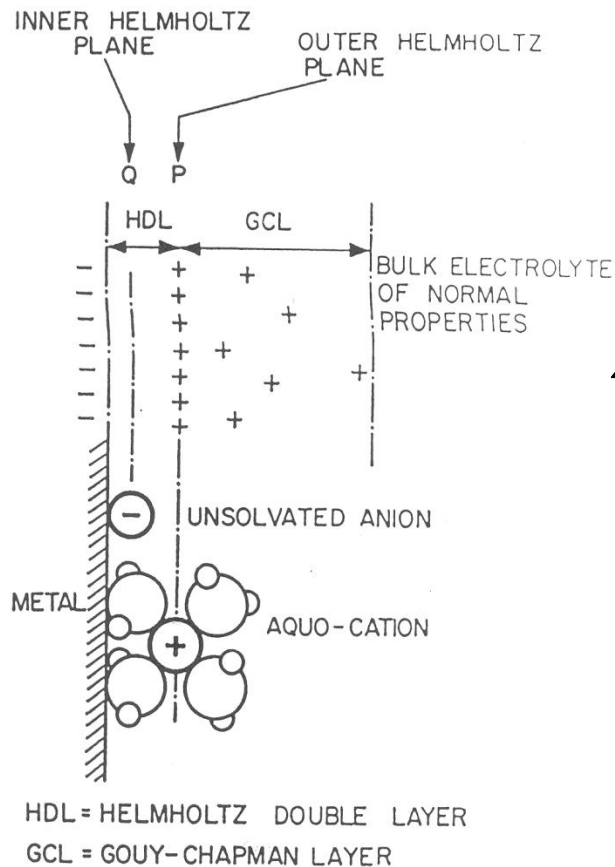
# AC Surface Layer Stirring Model

- Increases the exchange current density for the hydrogen cathodic half cell reaction on the Evan's diagram
- Amplifies the potential corrosion current.



**Effect of stirring in the exchange current density on both the reduction and oxidation half-cell reaction and the resulting shift in the corrosion rate (for a non-passive alloy).**

# Impedance Measurements for Stirring *Model 4*



Measurements will show magnetism affects corrosion rate; change of capacitance and/or inductance reveal location of corrosion

$$Z = \sqrt{R^2 + (1/\omega C)^2 + (\omega L)^2}$$

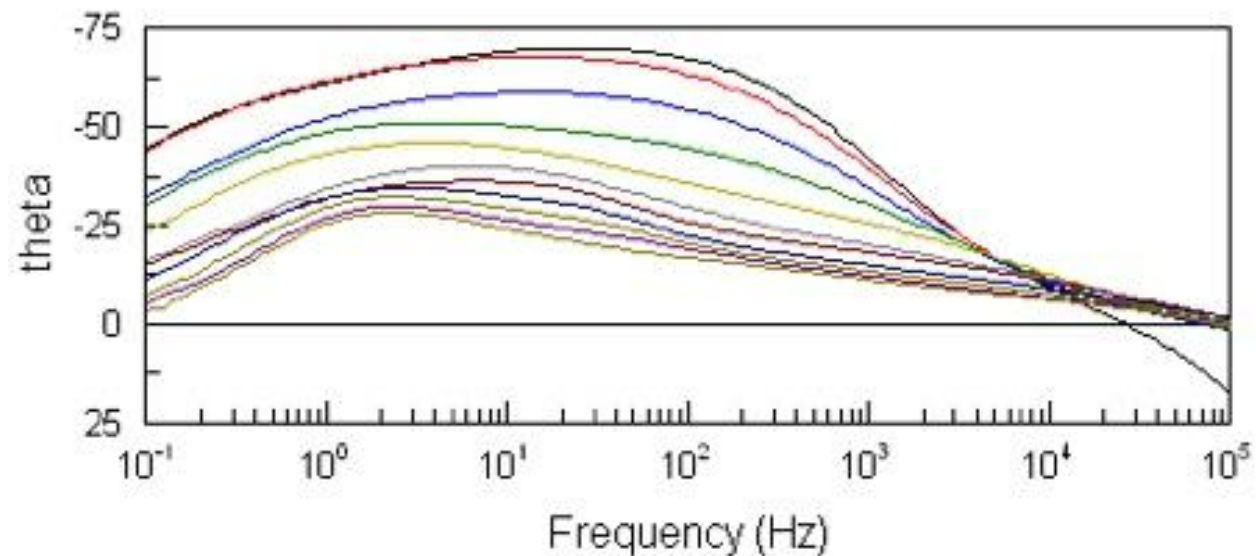
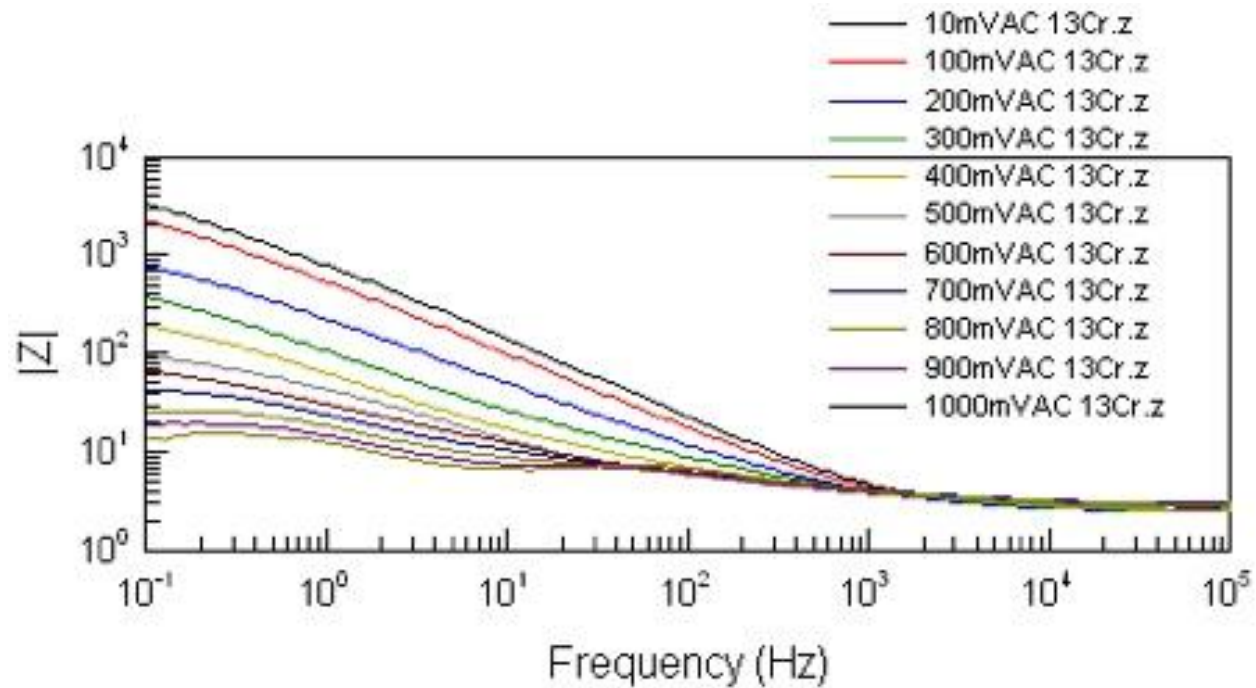
R is a function of the concentration of carriers and scattering in solution

C (Capacitance) is a function of the HDL strength

L (Inductance) is a function of the GCL

FIG. 1.4 The structure of the electrical double layer.

# Results- Electrochemical Impedance Spectroscopy



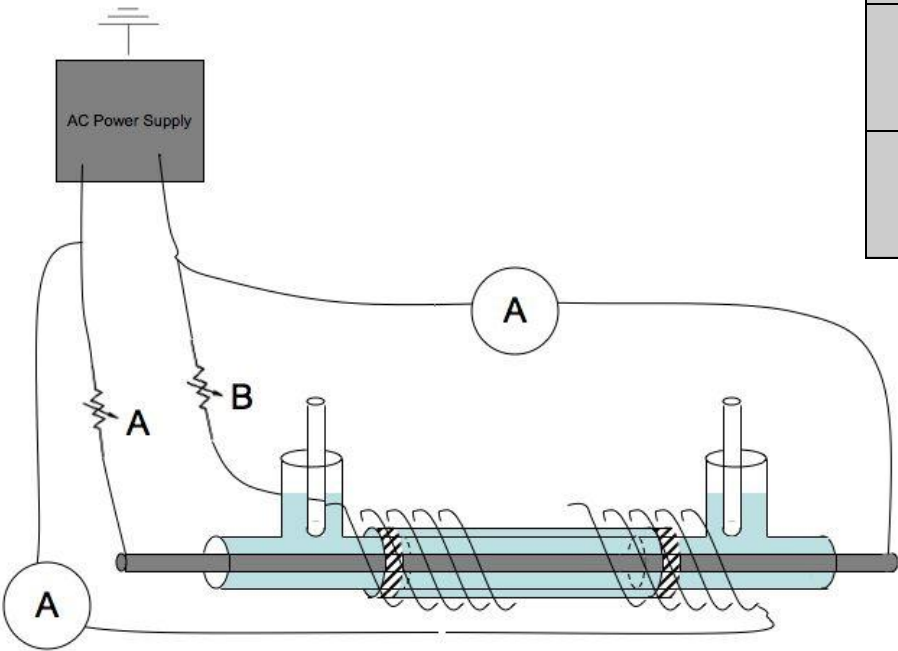
# Model Testing Matrix

<b>Model</b>	<b>Responsible Phenomena</b>	<b>Tested By:</b>
<b>Passive Layer Rectification</b>	<b>conduction</b>	<b>pitting and cracking assessment, potentiostat measurements</b>
<b>Surface Layer Stirring</b>	<b>induction</b>	<b>impedance measurements</b>
<b>Self-Biasing</b>	<b>induction and/or conduction</b>	<b>poteniostat measurements</b>
<b>Alkalization</b>	<b>induction</b>	<b>pH meter</b>

# Experimental Setup & Matrix

Experimental matrix showing the use of variable resistors to control amount and type of AC current experienced by sample for AC corrosion.

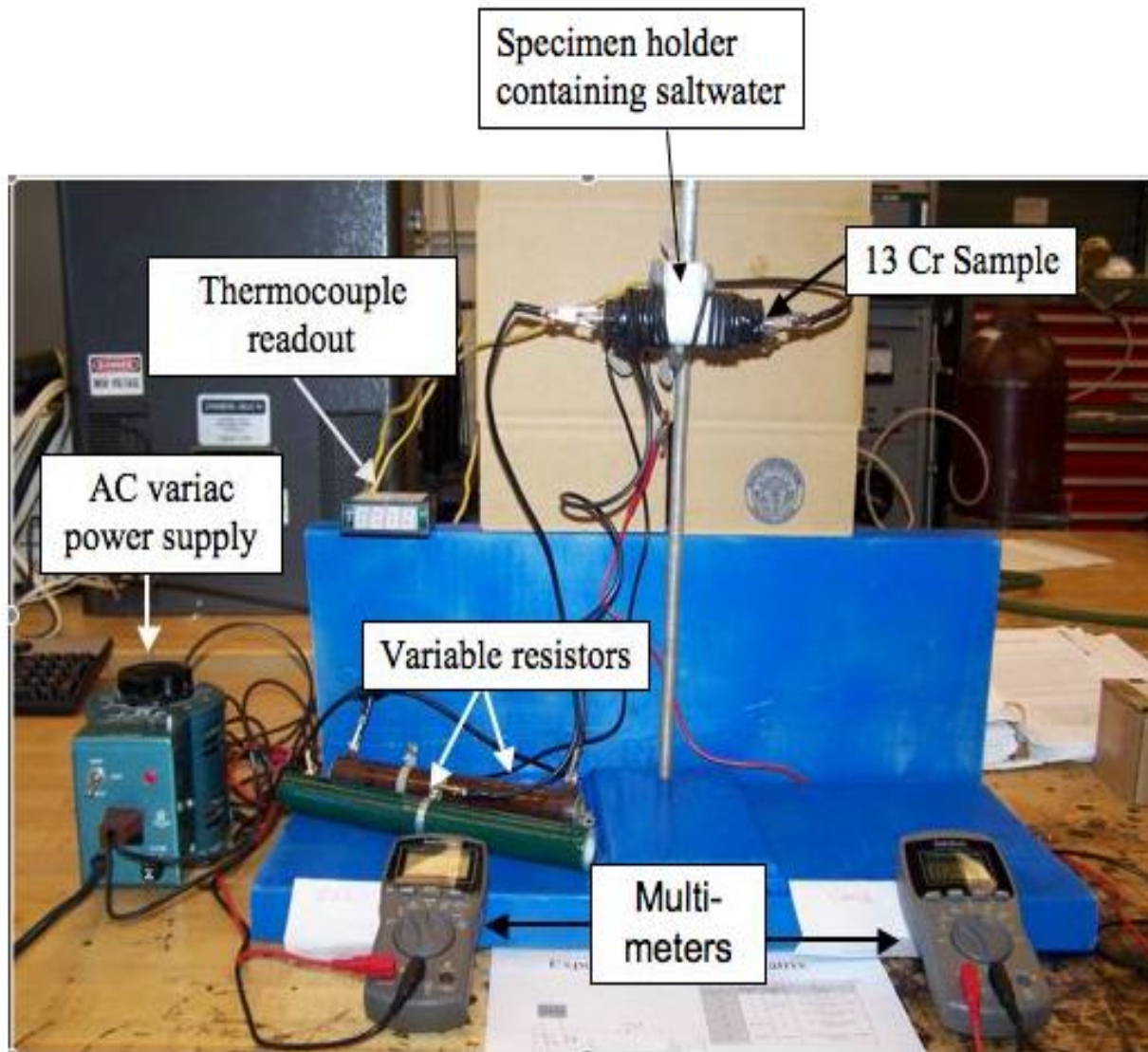
Configuration	Resistor A	Resistor B	Result
1	$\infty$	0	100% induction, no AC conduction
2	$\infty$	Variable	Variable induction, no AC conduction
3	0	$\infty$	No induction, 100% AC conduction
4	Variable	$\infty$	No induction, variable conduction
5	Variable	Variable	Variable induction, variable conduction



Experimental setup to test for AC corrosion mechanism



# Experimental Setup



# Super-martensitic stainless steel composition

Table 2. Composition (wt pct.) of Super martensitic stainless steel used in pipelines.

Analysis:	C	Mn	Si	Cr	Ni	Mo	Cu	N
Typical 13 Cr	<0.01	0.6	0.15	12	6-7	2.5	0.02	5.3
CSM analysis of Statoil pipe	0.008	0.41	0.26	12.00	6.4	2.2	0.06	6.40

- **Low carbon (<0.01):** allows the formation of a “soft” martensite that is more resistant than standard martensitic grades to hydrogen-induced cracking
- **Nickel:** promotes austenite formation and expands the gamma loop region of the phase diagram
- **Molybdenum:** improves corrosion resistance
- **Chromium :** marginal considering it takes 12 wt. pct. to achieve a self repairing stainless steel
- **Nitrogen:** eases formation of the low carbon martensitic structure in steel-making and strengthens steel

# Results- Pitting

Pit at 925X on 13Cr sample after 408 hours (17 days) test in artificial seawater under an applied AC of 8010 A/m<sup>2</sup>, showing resulting pitting typical over surface.

Det	WD	5/27/2008	HV	Spot	Mag
ETD	14.7 mm	1:52:48 PM	20.0 kV	4.0	925x

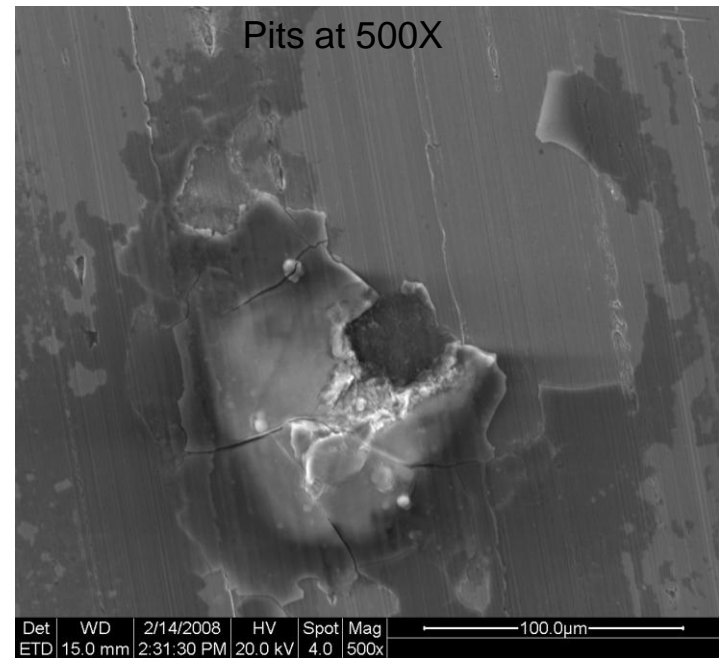
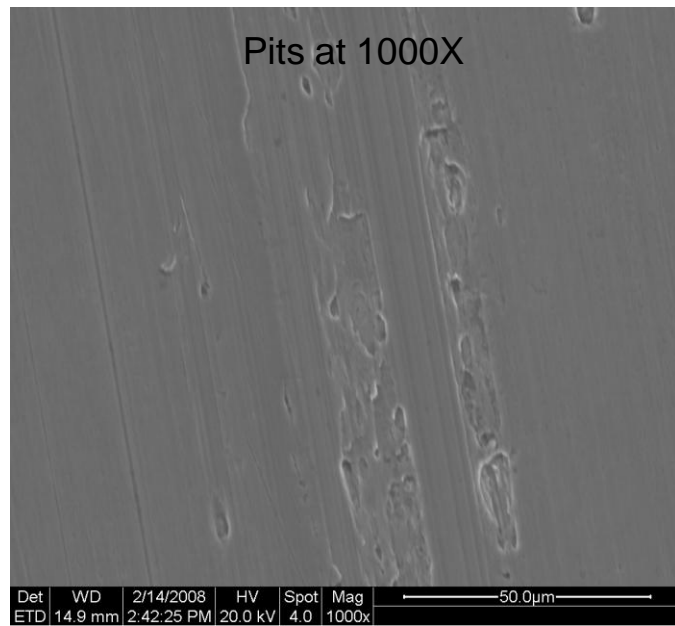
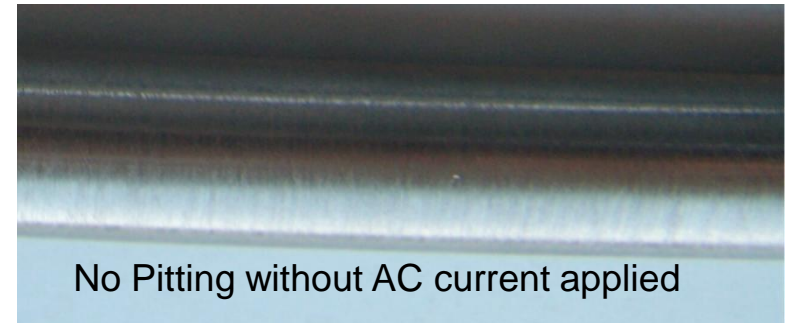
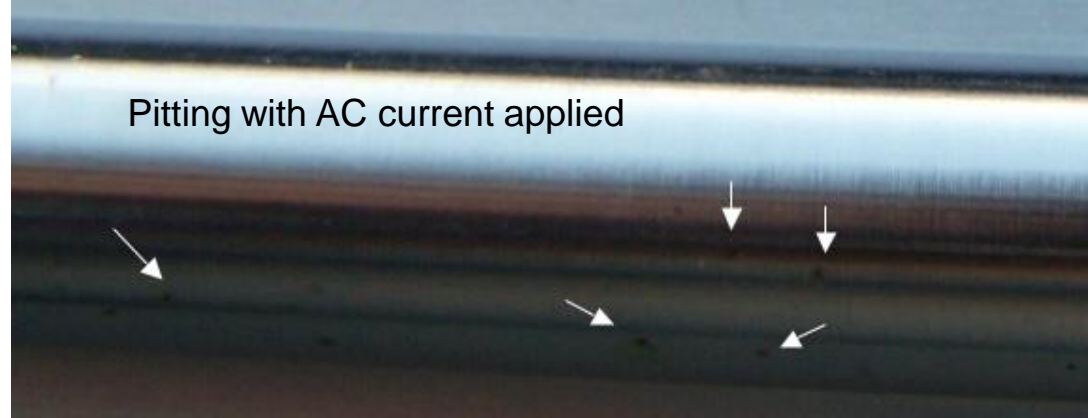
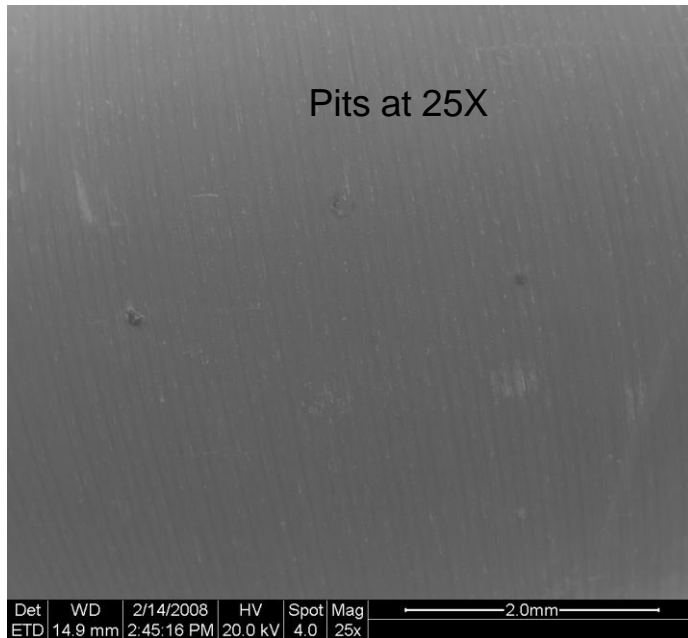
50.0µm

No Pitting observed at 50X following testing without AC current in solution for 17 days

Det	WD	2/14/2008	HV	Spot	Mag
ETD	15.0 mm	3:05:00 PM	20.0 kV	4.0	50x

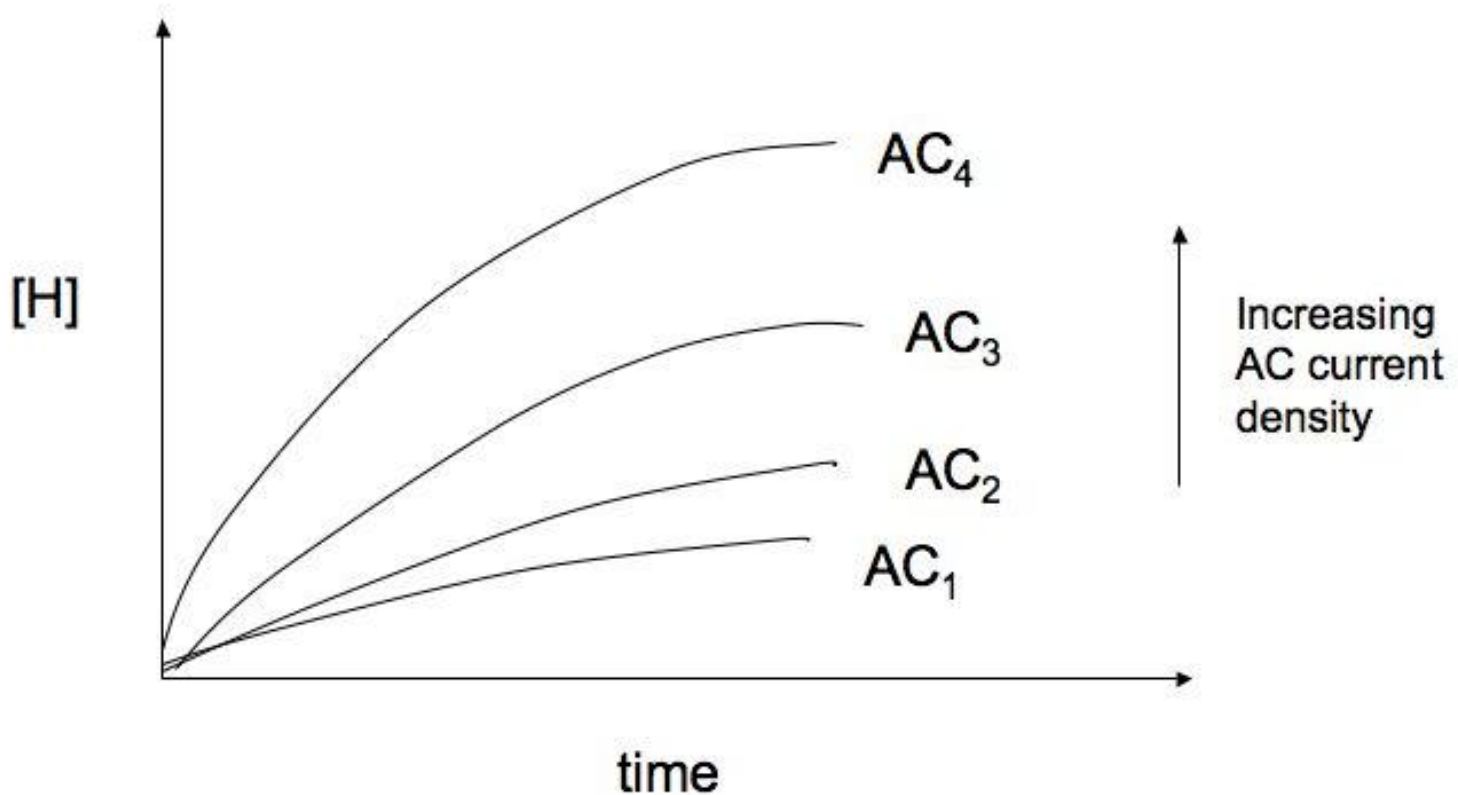
1.0mm

# Results- Pitting



# Proposed Effect on H Ingress

Can also have a cathode problem related to hydrogen generation



Schematic plot of possible effect of AC on hydrogen ingress in 13 Cr Super martensitic stainless steel.

# Summary

- **Results suggest the increased use of electric power in DoD applications requires a thorough understanding of AC corrosion.**

## Proposed Research

- **A Joint Industry Project is proposed to investigate the effects of AC corrosion on metallic structures and assemblies**
  - **The JIP will:**
    - » **verify the proposed models of AC corrosion**
    - » **develop analytical tools to assess the susceptibility to AC corrosion**
    - » **identify practices to assess and mitigate AC corrosion**
- **Separate AC corrosion projects can be established to investigate your specific needs**

# Acknowledgements

- DOI-MMS and DOT-PHMSA
- Jenny Collins for technical assistance
-

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# Fe-Cr Phase Diagram

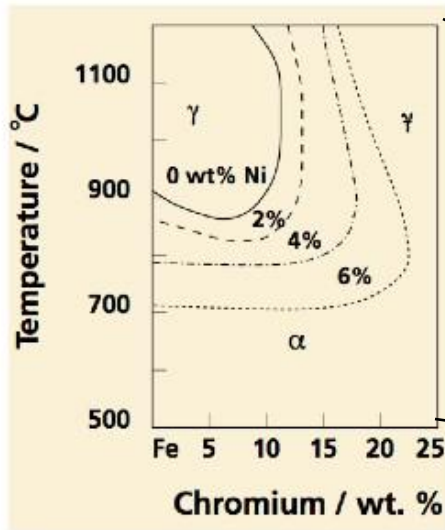


Figure 16. Effect of nickel on austenite stability field of the Iron-Chromium phase diagram (Carrouge, 2002).

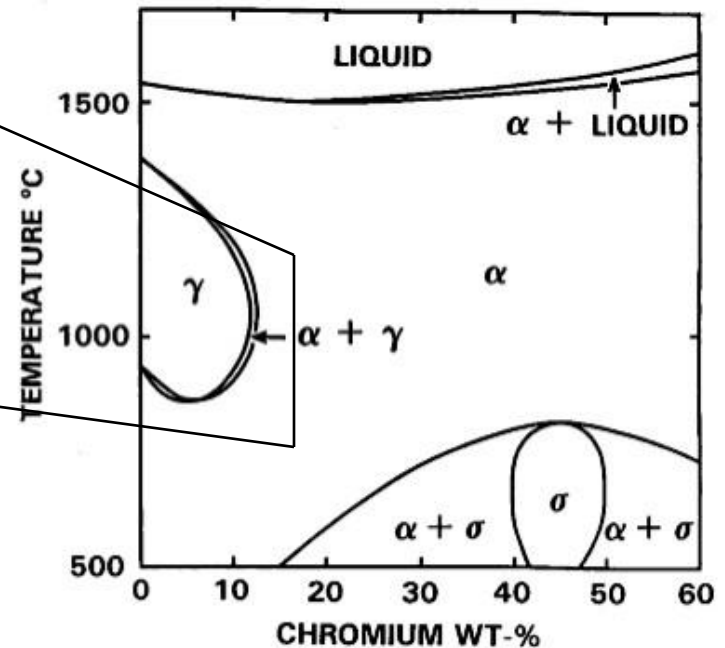
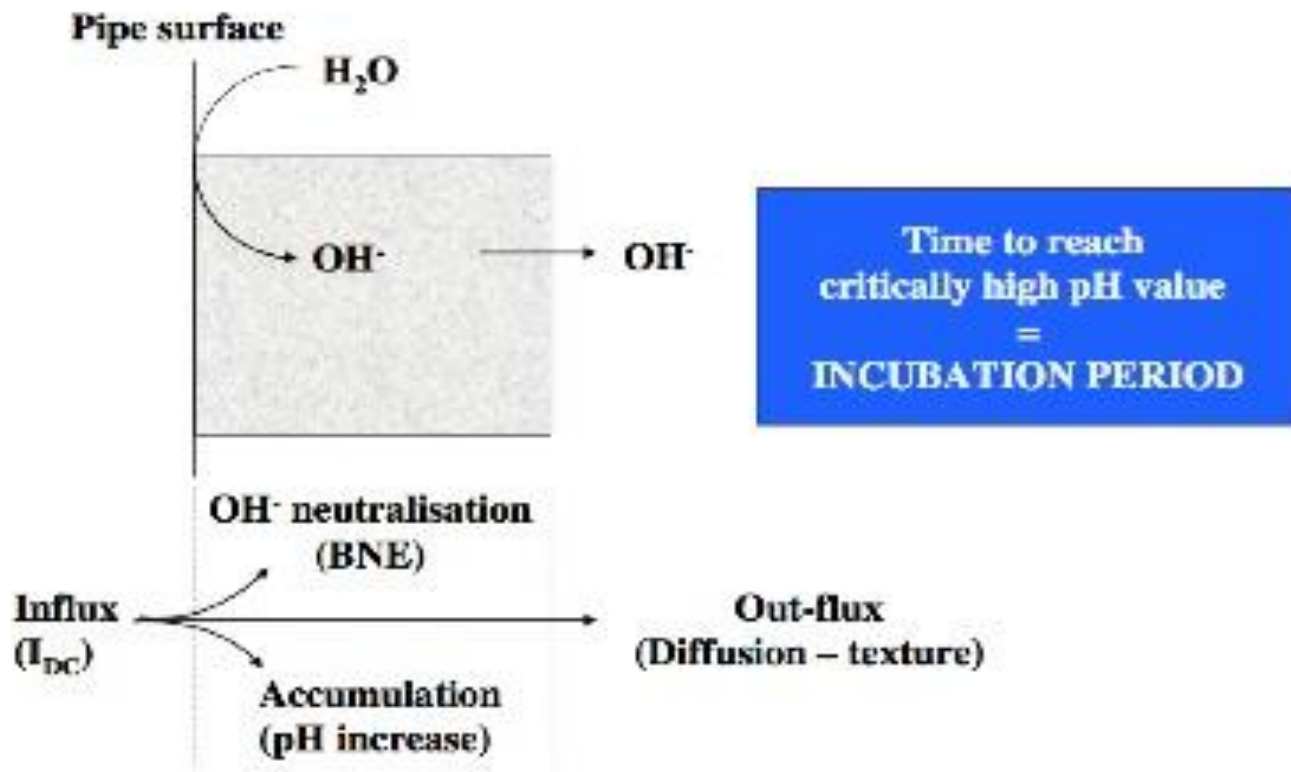


Figure 15. Iron-Chromium Phase Diagram (Talbot, 1998).

# Alkalization Model

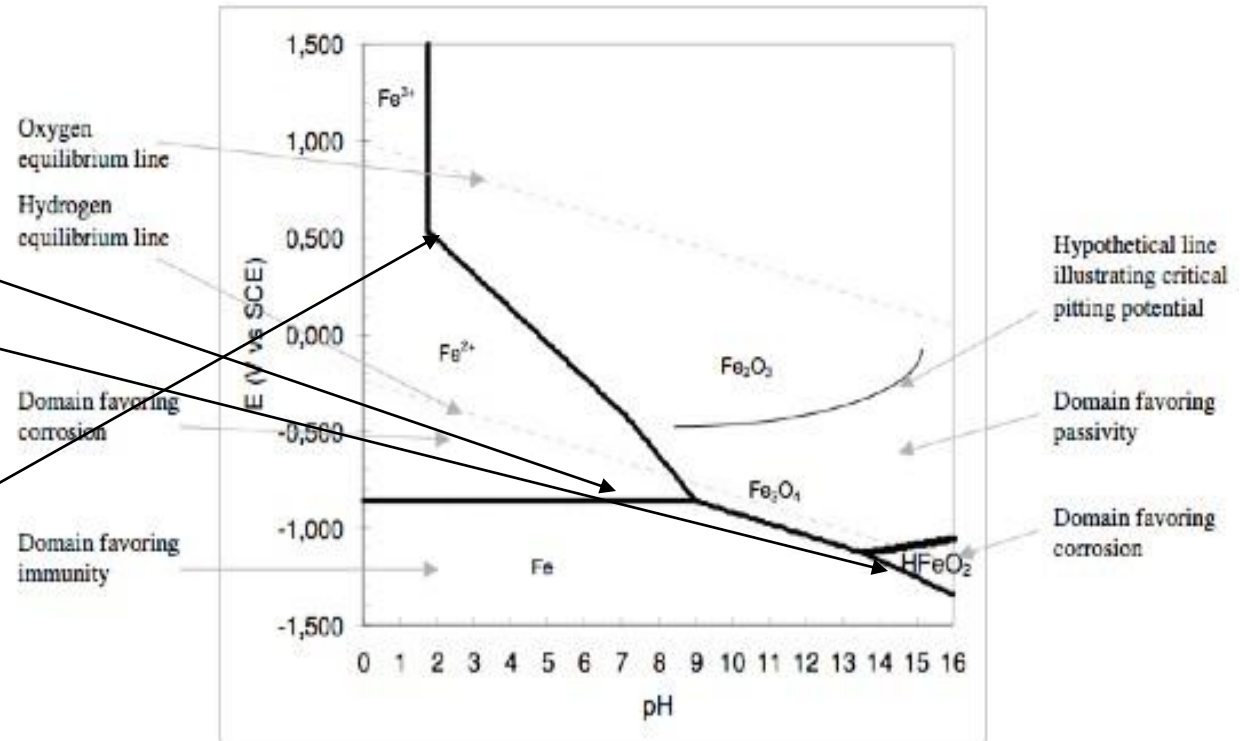
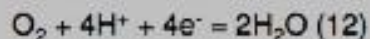
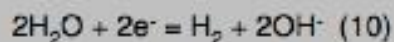
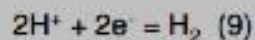
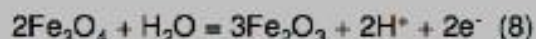
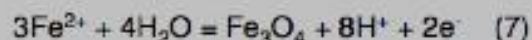
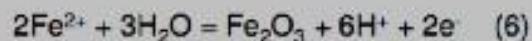
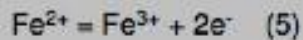
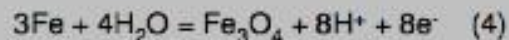
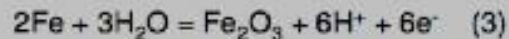
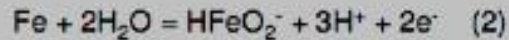
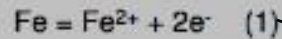
- AC stray current:  
Excess CP fatal  
due to an  
unexpected  
increase in pH at  
coating faults
- CP current  
increases hydrogen  
production which  
leads to production  
of  $\text{OH}^-$  ions  
(Galsgaard, 2006)



**Alkalization model for AC corrosion, where pH is increased at a cathodically protected surface (Galsgaard, 2006).**

# Pourbaix Diagram and AC Corrosion

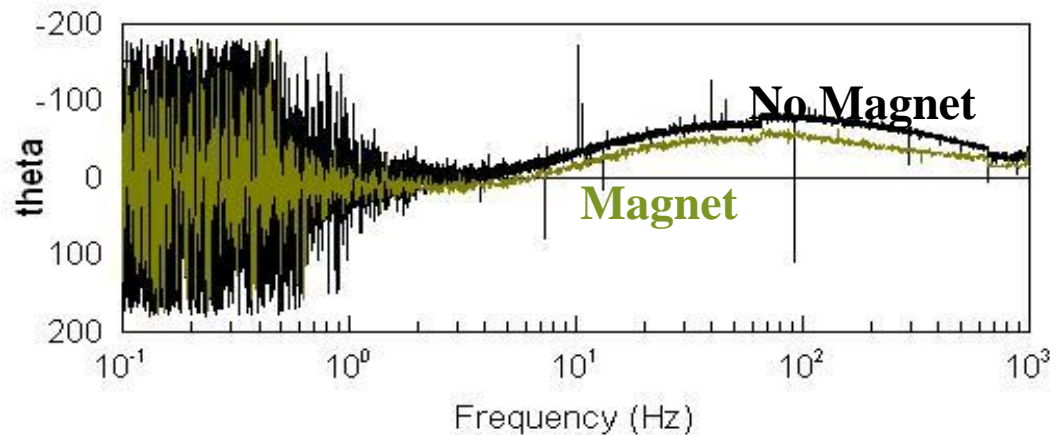
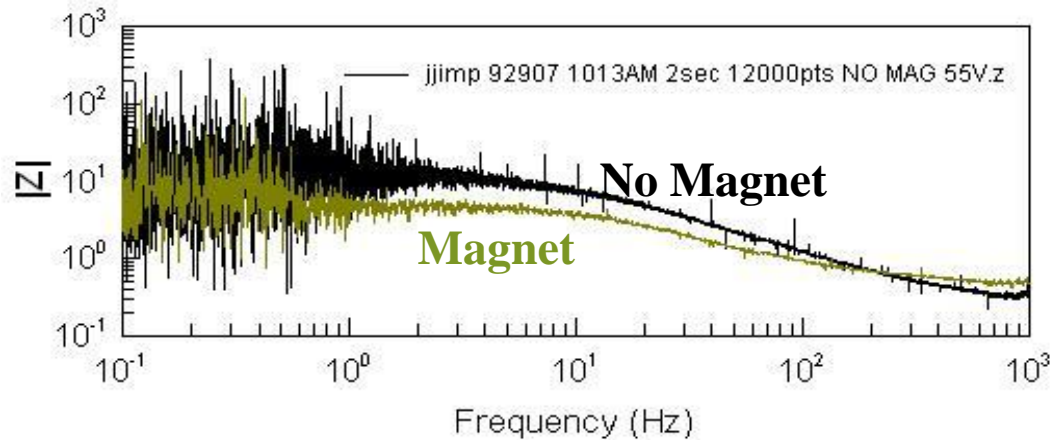
Electrochemical reactions relating to the Pourbaix diagram of iron in water.



Pourbaix diagram for iron in water, based on theoretical calculations of the thermodynamics of electrochemical reactions.

# Impedance Measurements

Measurements indicate a significant change in both impedance and capacitance with the addition of magnetic fields



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